

Dissociation of singlet excitons dominates photocurrent improvement in high-efficiency non-fullerene organic solar cells

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January 28, 2023

Abstract

In organic solar cells, the singlet and triplet excitons dissociate into free charge carriers with different mechanisms due to their opposite spin state. Therefore, the ratio of the singlet and triplet excitons directly affects the photocurrent. Many methods were used to optimize the performance of the low-efficiency solar cell by improving the ratio of triplet excitons, which shows a long diffusion length. Here we observed that in high-efficiency systems, the proportion of singlet excitons under linearly polarized light excitation is higher than that of circularly polarized light. Since the singlet charge transfer state has lower binding energy than the triplet state, it makes a significant contribution to the charge carrier generation and enhancement of the photocurrent. Further, the positive magnetic field effect reflects that singlet excitons dissociation plays a major role in the photocurrent, which is opposite to the case of low-efficiency devices where triplet excitons dominate the photocurrent.

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Keywords: polarized light, organic solar cell, high efficiency, singlet/triplet exciton.

Abstract

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1. Introduction

In recent years, spintronics has become an emerging discipline in materials physics. Through realizing the measurement and regulation of the spin state, many new phenomena, which could provide a new scheme to optimize the related devices, were observed.^[1-5] Manipulating spin statistics is usually achieved by applying external field regulations such as electric, magnetic, and optical fields in many organic devices.^[1, 6-8] In the photovoltaic sector, the organic solar cells (OSCs) performance can be improved by singlet fission or control of the spin-orbital effect.^[9, 10] The external magnetic field mainly changes the ratio of singlet and triplet in the excited state in two ways: the magnetic field effect in the formation of the excited state and the intersystem crossing caused by the magnetic field.^[11] However, the role of singlet and triplet excitons in contributing to photocurrent in OSCs seems unclear. Hence, figuring out the effect of singlet and triplet excitons on photocurrent is a meaningful direction for profoundly understanding the mechanism of OSCs.

Since the exciton binding energy in organic semiconductors is large at room temperature,^[12] its excited state forms an intramolecular excited (Frenkel exciton)^[13] or intermolecular excited state (Wannier excitons).^[14] The spins of electrons have multiplicity, and both electrons and holes in the excited state have spin-antiparallel (singlet) and spin-parallel (triplet) states. With the help of hyperfine interaction and spin-orbit coupling effects, singlet and triplet excitons could be converted into each other.^[15] In the domain of OSCs, the short diffusion length (LD) of the exciton is the main limiting factor to the effective charge carrier separation.^[16] Because the LD of triplet exciton is longer than that of singlet exciton, increasing the ratio of triplet exciton helps enhance the PCE of OSCs. Therefore, many methods have been reported to increase the proportion of triplet excitons through orbital coupling effects, such as introducing heavy metal molecules or atoms.^[1, 9, 17] The above conclusions are all summarized in the devices with a low-efficiency system. In 2020, Hu et al. proved that the dipoles in the non-fullerene acceptor molecule could be polarized by light excitation, which makes the excited state easier to separate into free charge, thus inducing the high efficiency in the non-fullerene system.^[18] However, in this high-efficiency system of OSCs, rare attention focuses on investigating the effect of the exciton spin state on the photocurrent by polarized light. It is worth reconsidering the function of singlet and triplet excitons in contribution to photocurrent for the following reasons. First, if the uniform dispersion of the bulk heterojunction can guarantee the efficient diffusion of singlet excitons to the interface, then increasing the proportion of triplet states may not be highly important. In addition, the exciton binding energy of the charge transfer (CT) triplet state is higher than that of the singlet CT state. Increasing its proportion in excitons may not necessarily contribute to improving photocurrent.

Based on the above analysis, we investigated the photocurrent responses of high-efficiency OSCs under different polarizations of light and analyzed the contributions of triplet excitons and singlet excitons to the current. Here, we found that the separation of singlet excitons plays a major role in the photocurrent, which is different from the case of a low-efficiency system. In the organic solar cells with PBDB-TF and IT-4F as active layers, an anisotropic axis was confirmed in as-prepared samples by changing the incident azimuth angle and the azimuth angle of the sample. The variable power and the external bias test further prove that the singlet exciton ratio generated under linearly polarized light excitation is improved, inducing a higher photocurrent. On the other hand, the circularly polarized light increases the proportion of triplet excitons, which is not conducive to the direct dissociation of charges. A similar trend is observed on the D18:Y6 OSCs with a power conversion efficiency (PCE) of 17.35%. The positive correlation between photocurrent and magnetic field indicates that the free charge in the high-efficiency device mainly comes from the direct dissociation of the singlet excitons.

2. Results and Discussion

2.1 Device characterization

The device structure used in the experiment is ITO/PEDOT:PSS/active layer/PFN-Br/Al and the active layer is PBDB-TF:IT-4F. **Figure 1** a shows the molecular formula of PBDB-TF and IT-4F. As shown in Figure 1b, the SEM cross-sectional picture presents the thickness of each layer of the device. The favorable continuity of each layer reduces the leakage current in the device, which is necessary for the regular operation of the device. Figure S1a shows the J-V curve of the solar cell. The corresponding IPCE spectrum and the integrated current obtained by IPCE are given in Figure S1b. The short-circuit current density (J_{sc}) of the cell is 20.12 mA/cm², and the obtained PCE can reach 13.12%.

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Figure 1. (a) The schematic diagram of the molecular structures of PBDB-TF and IT-4F. (b) SEM image of the device cross-section. GIWAXS spectra of (c) PBDB-TF, (d) IT-4F, (e) PBDB-TF:IT-4F films. (f) The Raman intensity in wavenumber 1430 cm⁻¹ with different polarized angles.

To gain a deep understanding of the effect of polarized light on device performance, it is necessary to investigate the morphology and anisotropy of the active layer. As shown in Figure 1c-e, we performed 2D-GIWAXS tests on PBDB-TF, IT-4F, and PBDB-TF:IT-4F films, respectively. For the single-component PBDB-TF, the characteristic peak (010) intensity is concentrated and has high crystallinity. At the same time, the π - π stacking is along the direction perpendicular to the substrate, forming a face-on orientation.^[19] However, the single-component IT-4F has a ring-shaped scattering feature, indicating that the single IT-4F molecules are randomly oriented.^[20] For the binary blend film, the orientation is similar to that of PBDB-TF, indicating that the alignment and orientation of organics are greatly affected by the polymer in the active layer of the prepared device. Meanwhile, the random packing of IT-4F molecules is suppressed, but the overall molecular stacking is still face-on, which is beneficial to the charge transport in the device.

2.2 The photocurrent response under polarized light

The single-component PBDB-TF and IT-4F were fabricated into the device. The polarized photocurrent tests are used to verify the effect of different stacking morphologies of molecules on the response of the device under polarized light. Figure S2a and S2c are the photocurrent curves of PBDB-TF and IT-4F obtained by adding 1/2 wave plate separately. It can be seen that the photocurrent signal of PBDB-TF changes periodically with the polarization angle of the 1/2 wave plate. However, the photocurrent signal of IT-4F does not change periodically. The single attenuation trend of the signal is caused by the intensified phase separation of small organic molecules under illumination. These results are similar to those obtained by GIWAXS spectra. And the films are anisotropic due to the ordered arrangement of the donor PBDB-TF, while the IT-4F films are isotropic due to the random orientation. After adjusting the angle of the 1/2 wave plate, a 1/4 wave plate is added to study the difference between the linearly and the circularly polarized photocurrent. As shown in Figure S2b and S2d, it is worth noting that the linearly polarized photocurrent of single-component PBDB-TF is larger than the circularly polarized photocurrent. In contrast, the photocurrent generated by IT-4F under differently polarized light is hard to observe.

Generally, the active layer thin films in OSCs are optically isotropic^[21] because the active layer is usually a bulk heterojunction. When changing the incident azimuth angle, however, it is found that the photocurrent signal changes with the variation of incident angles, as shown in **Figure 2** a. To further verify whether the thin film has anisotropy, we tested it by changing the azimuth angle of the sample in Figure 2b. The sample shows an anisotropy axis through the above two-step experiments.

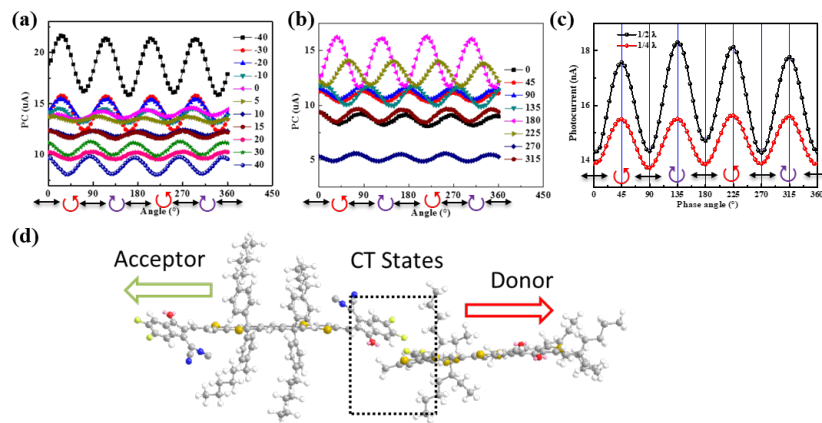


Figure 2. (a) The relationship of photocurrent with different incident angles. (b) The relationship of photocurrent with different azimuth angles. (c) Photocurrent measured by switching phase angle under 1/2 wave plate and 1/4 wave plate. (d) The schematic of the CT states.

In addition, we performed a polarization Raman test on the active layer film to further verify their anisotropy. Figure S3a shows the relationship between the angle (between the polarization direction of the excitation light and the optical axis direction) and the intensity of the polarization Raman scattering spectrum of the sample, where the rotation angle changes from 0° to 360° , and the measurement range locates in $1250\sim 1650\text{ cm}^{-1}$ wave number. At the wave number of 1430 cm^{-1} , the peak intensity varies periodically with the angle, as shown in Figure 1e. According to previous studies,^[22, 23] this wavenumber is the Raman scattering peak of thiophene, which is consistent with the conjugated structure in our conjugated polymer.

Since the polarization photocurrent test cannot be performed by the reported method,^[24] the anisotropy axis of the film must be verified before the polarized light passes through the 1/4 wave plate. First, a 1/2 wave plate was placed between the polarizer and the sample to explore the anisotropy axis of the film, as shown in Figure 2c. Adjusting the 1/2 wave plate to the direction of the anisotropy axis of the sample, a periodic function of 90° can be seen. Then the 1/4 wave plate is placed between the 1/2 wave plate and the sample, and the 1/4 wave plate is in the state of circularly polarized light when the phase angle is 45° . By measuring the difference between the phase angle of 45° and 0° , the difference of the 1/2 wave plate is two times that of the 1/4 wave plate, which is consistent with our assumption. To exclude the influence of sample anisotropy and accurately measure the difference between the circularly polarized photocurrent signal and the linearly polarized photocurrent signal, we rotated the fixed 1/2 wave plate by 22.5° . The difference between the photocurrent signals of circularly polarized light and linearly polarized light can be obtained.

To demonstrate the reliability of our testing method, we apply this method to standard Si solar cell testing, as shown in Figure S4a. First, only the 1/2 wave plate was added for testing, and the polarization direction of the linearly polarized light was changed by rotating the 1/2 wave plate. It is found that the photocurrent signal of the Si cell does not change with the polarization angle. In Figure S4b, the 1/4 wave plate was added between the 1/2 wave plate and the sample, and the 1/2 wave plate was fixed for testing. The photocurrent signal also did not change with the polarization angle of the 1/4 wave plate. It is well known that standard Si cells are optically isotropic. Therefore, the photocurrent should also not vary with the polarization angle of the 1/2 wave plate, which agrees with our experiments. Moreover, the polarized light would not affect the photocurrent because the photogenerated exciton with lower binding energy dissociates into free charge efficiently enough in silicon solar cell.^[25]

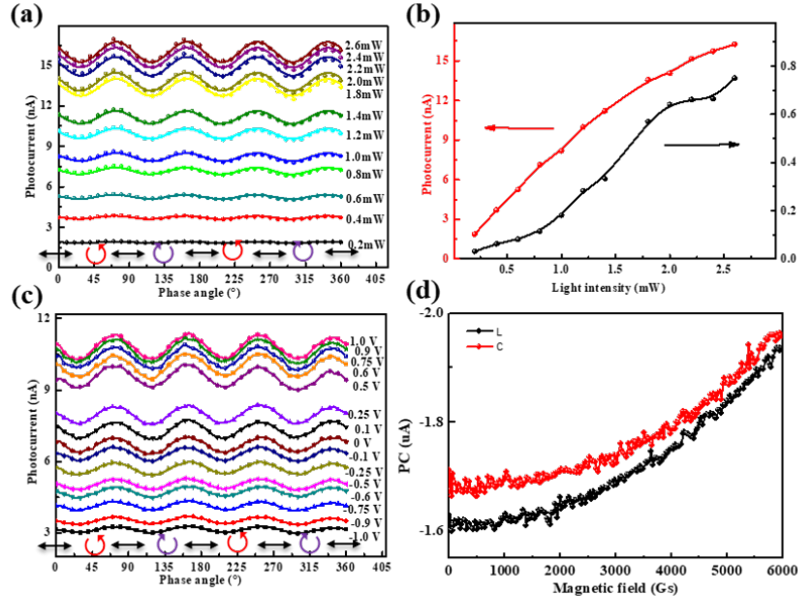


Figure 3. (a) Photocurrent measured by switching phase angle with different laser power. (b) The relationship of PC and ΔPC with different laser power. (c) Photocurrent measured by switching phase angles with different applied voltages. (d) Linearly and circularly polarized photocurrents in magnetic fields vary with the magnetic field. The symbol arrow and circular arrow represents the linearly and circularly polarized light.

Based on the anisotropy analysis of the thin organic film, we tested the polarized photocurrent to study the photoelectric process of the excited state of the active layer in OSCs. As shown in **Figure 3 a**, the photocurrent signal of the sample changes periodically with the angle of the $1/4$ wave plate. The variation of photocurrent has the same trend in the power range from 0.2 mW to 2.6 mW. Compared with linearly polarized light excitation, the signal could be attenuated to a certain extent under circularly polarized light excitation. To quantitatively compare the difference between the linearly polarized photocurrent and the circularly polarized photocurrent, we define PC as the average photocurrent, ΔPC as the difference between the linearly polarized photocurrent and the circularly polarized photocurrent, PC(L) as the linearly polarized photocurrent, PC(C) as the circularly polarized photocurrent. Then we extract the variation trends of PC and ΔPC with light intensity. As shown in **Figure 3b**, PC shows an increasing linear trend with the rise of optical power. At higher optical

2.3 Discussion

There are two hypotheses for why ΔPC varies with optical power: 1) The electrical and optical properties of nonmagnetic organic semiconductors respond strongly to an applied magnetic field, known as organic magnetic field response (OMFE). The difference between linearly and circularly polarized light could arise from the spin state change due to the electric field component of circularly polarized light, thereby generating an equivalent magnetic field (the inverse Faraday effect).^[26] The generated equivalent magnetic field can modulate the electrical properties of the active layer of the device, resulting in different signal responses under different polarization states.^[27] 2) The circularly polarized light directly transfers the photon angular momentum to the electrons in the active layer to polarize the excitons, resulting in a spin-orbit coupling effect, thereby changing the conversion process of singlet excitons and triplet excitons, inducing the change ΔPC .^[28,29] Relative to assumption 1), if there is an equivalent magnetic field, ΔPC should have a quadratic relationship with optical power,^[30] which is inconsistent with our linear relationship; therefore, assumption 2) is the most probable under our system.

In perovskite materials, due to the presence of heavy metal elements such as Pb or Sn, there is a strong spin-orbit coupling effect under polarization conditions.^[31,32] While organic semiconductor materials are mainly composed of light elements, it is believed that there should be no internal spins-orbit effect. However, in organic conjugated polymers with larger molecular scales, atomic orbitals can be converted into molecular orbitals. When high-energy electron excitation or injection makes the electron occupy the excited state, the electron has a considerable orbital angular momentum, and the spin-orbit effect also occurs at this time.^[33,34]

Due to the law of spin selection, only singlet excitons can be generated by light absorption in the active layer, and singlet excitons can be converted into triplet excitons through intersystem jumping.^[35] The binding energy of excitons at room temperature is large and cannot be directly separated. Singlet excitons and triplet excitons can dissociate into singlet charge transfer (CT) and triplet CT states, respectively, as shown in Figure 2d. The singlet CT state has lower binding energy than the triplet state and thus significantly contributes to the charge carrier generation.^[36] By increasing the optical power, the number of excited states in the active layer can be effectively improved. The spin-orbit coupling effect of circularly polarized light produces more triplet excitons, which is not conducive to direct dissociation to generate charges. Therefore, ΔPC increases with the increase of light intensity.

Next, we studied the relationship between the polarized photocurrent and the applied voltage of the organic solar cell. The excitation light still chooses the polarized light of 532 nm, and the voltage range is -1 V to 1 V. As shown in Figure 3c, the PC signal increases with the increase of the applied bias voltage. And the average PC and ΔPC are extracted and plotted in Figure S5a. It can be seen that ΔPC also has a slightly increasing trend with the increased applied bias voltage. Since the applied bias voltage increases the dissociation rate of the singlet CT state, the current would increase with the applied bias voltage. Under the same bias voltage, the linearly polarized photocurrent is still larger than the circularly polarized photocurrent, indicating that there are more singlet excitons excited by linearly polarized light than those excited by circularly polarized light, which is consistent with the conclusion obtained from the variable power test.

In organic semiconductor materials, the magnetic field effect of photocurrent is easy to observe and can be used as an effective means to study the conversion process of singlet and triplet excited states in organic solar cells.^[37] The working process of organic solar cells mainly includes four processes: light absorption, generation of excited states, separation of excited states to generate electrons and holes, charge transport in the active layer, and collection by the positive and negative electrodes. Among them, the magnetic field effect mainly occurs in the process of separation of excited states to generate electrons and holes. There are two main ways to generate a charge from the excited state. One is the direct dissociation of the excited state to generate electrons and holes, and the other is the collision reaction between the excited state and the charge. Because the singlet has a much larger dissociation rate than the triplet, the excited state dissociation, which is essentially driven by the electric dipole-dipole interaction between the molecules, is mainly participated by the singlet state. The reaction between the excited state and the charge is essentially coulomb scattering. Due to the long lifetime of the triplet state, the reaction mainly involves the triplet state. The triplet state excitons can collide with the charges in the trap and free charges to generate new electron-hole pairs.^[17]

The applied magnetic field can affect the above two processes by changing the ratio of singlet/triplet excitons and the rate of excited state-charge reaction through the magnetic field response. However, the magnetic field has different effects on these two processes. On the one hand, the external magnetic field can increase the number of singlet CT states through the intersystem jumping of the magnetic field response so that the current increases with the magnetic field increase.^[38] On the other hand, an external magnetic field can weaken the triplet excitons-charge reaction by degenerating the triplet excitons. As a result, the current decreases with the magnetic field increase.^[39]

Further, we excite the samples with different polarized lights under the magnetic field condition and observe the experimental phenomenon. Figure 3d shows the variation of the linearly and circularly polarized photocurrent signals with the magnetic field intensity. The magnetic field positively affects the polarized photocurrent, and the result indicates that the dissociation of the singlet CT state dominates the system in our study. The magnetic field increases the ratio of the singlet state to the triplet state by disturbing the

intersystem crossing between the singlet state and the triplet state of the excited state, thereby increasing the current. The linearly polarized light is more affected by the magnetic field, which proves that there are more singlet excitons in the system under the excitation of linearly polarized light. After that, we performed Lorentzian fitting and normalization of the data to obtain Figure S5b. In the process of changing from circularly polarized light to linearly polarized light, the peak shape narrows, and the half-peak width decreases from 515 mT to 435 mT. Generally, the narrower the peak shape indicates the higher the proportion of singlet CT states.^[40] This proves that circularly polarized light increases the ratio of triplet excitons, which is not conducive to separation to generate charges.

Through testing in a magnetic field, circularly polarized light can increase the proportion of triplet excitons because circularly polarized photocurrent directly transfers angular momentum to organic semiconductors through the spin-orbit coupling effect. Manipulating

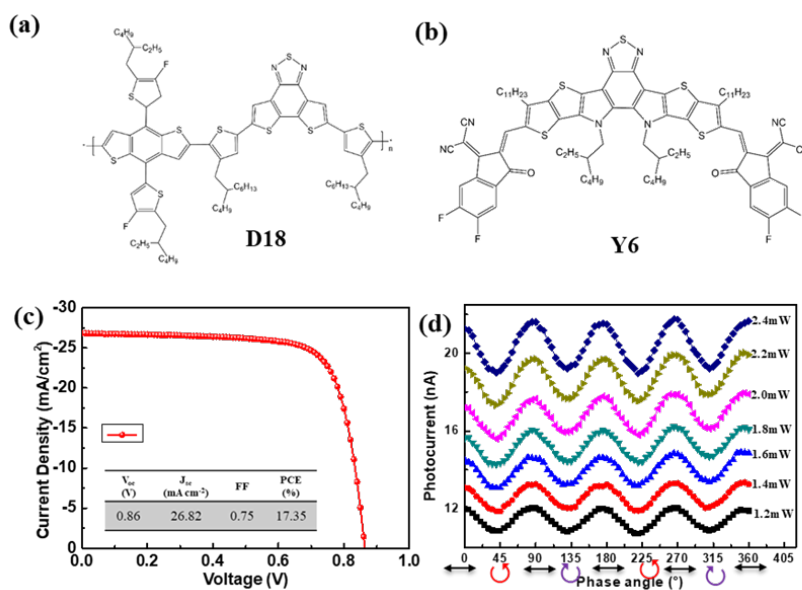


Figure 4. The molecular structures of D18 (a) and Y6 (b). (c) the I-V curve of the best device. (d) Photocurrent measured by switching phase angles with different laser power.

spins in organic solar cells and exploiting triplet excitons can help us gain insight into the excited state and charge transport processes in organic photonic devices.

In order to further prove whether this phenomenon can be observed in other systems, the device of the current highest efficiency system with the active layer D18:Y6 was prepared. The schematic molecular structure of the donor and acceptor is shown in **Figure 4** a and b. The exploration of the annealing process shows that the efficiency of the D18:Y6 system decreases after annealing, which is different from the previous system. To make the acceptor distribution in the active layer more uniform, we perform solvent annealing without heating. The effect of solvent annealing time on device performance was studied, and a device with an energy conversion efficiency of 17.35% was finally prepared (Figure 4c). We carried out the polarization photocurrent test on the prepared high-efficiency device and obtained similar results as PBDB-TF:IT-4F, which also has periodic changes, and the linearly polarized photocurrent effect is greater than the circularly polarized photocurrent effect, as shown in Figure 4d. This indicates that the polymer with a large conjugated structure has a spin-orbit coupling effect under polarized light conditions. By adjusting the polarization conditions of the excitation light, the ratio of singlet and triplet excited states in the active layer can be changed, thereby generating different photocurrent signals..

3. Conclusion

In summary, we investigated the effect of the exciton state on photocurrent in the organic solar cell by manipulating the spin state of the excited exciton with different polarization light and varied external magnetic fields. In the PBDB-TF:IT-4F system, the photocurrent signal under linearly polarized light is larger than that of circularly polarized light. Because the circularly light would increase the ratio of triplet exciton and the singlet charge transfer state has lower binding energy than the triplet state, the singlet exciton plays the primary role in photocurrent. The varied power and bias voltage test certify that the ratio of singlet exciton would increase under the linearly polarized light, thus improving the photocurrent. Combined with the magnetic field photocurrent response, the narrower peak of the normalized profile reflects that the contribution of free charge is mainly from the direct dissociation of the singlet CT state. The identical trend was also observed in the D18:Y6 system, which possesses the highest PCE in organic solar cells. This result is entirely different from the case of a low-efficiency system, where the main contribution to the photocurrent comes from the triplet excitons. Our findings provide a new explanation for the high PCE in OSCs devices and pave the way for further improving the performance by manipulating the spin state of the exciton.

4. Experimental Section

4.1 Materials and Solution Preparation

PBDB-TF, and ITIC-4F, were purchased from 1-Material. PC₆₁BM was purchased from Nano-C. The PEDOT:PSS was purchased from H.C. Starck Clevios. PFN-Br was purchased from SolarMar Inc. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.9%), ethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$, 99.5%) and 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$, >99.8%) were purchased from Sigma Aldrich. All the materials and solvents were commercially available and used without further purification. PBDB-TF and ITIC-4F were dissolved (1:1, wt%) in a mixed solution of chlorobenzene and 1,8-diiodooctane (99.5:0.5, vol%).

4.2 Device Fabrication

First, the ITO substrates were sequentially cleaned ultrasonically in deionized water, acetone, and isopropanol. The substrates were treated with UV-ozone for 15 min before spin-coating. After that, PEDOT:PSS was spin-coated on the ITO surface at 5000rpm and then annealed at 160 for 15 min in an ambient atmosphere. These samples were transferred into a glove box under a nitrogen atmosphere immediately. The active layer solution was then spin-coated at 3000 rpm to obtain a film thickness of about 100 nm. The film was then annealed at 100 for 10 min. Then the cathode buffer layer of PFN-Br (about 5 nm) was spin-coated onto the active layer at 3000 rpm for 30 s. Finally, about 100 nm Al was deposited by thermal evaporation as a cathode under vacuum at a pressure of about 2×10^{-4} Pa.

4.3 Characterization

GIWAXS images were acquired by using a Xeuss WAXS system, and the active layers were deposited on the Si substrates. The linearly polarized laser beam of 520 nm with about a 2 mm diameter was combined with a $1/2$ wave plate and a $1/4$ wave plate to generate a switchable linearly and circularly polarized laser. Magneto-photocurrent was performed by recording photocurrent as a function of the magnetic field which was applied parallel to the sample plane.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This study was financially supported by the National Key Research and Development Program of China (Grant No. 2018YFE0204000), the National Natural Science Foundation of China (Contract Nos. U20A20206, 51972300, 62274155 and 21975245), the Strategic Priority Research Program of the Chinese

Academy of Sciences (Grant No. XDB43000000), and the Key Research Program of Frontier Science, Chinese Academy of Sciences (Grant No. QYZDBSSW-SLH006). K. L. appreciates the support from the Youth Innovation Promotion Association, the Chinese Academy of Sciences (No. 2020114), and the Beijing Nova Program (No. 2020117).

Received: ((will be filled in by the editorial staff)) Revised: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

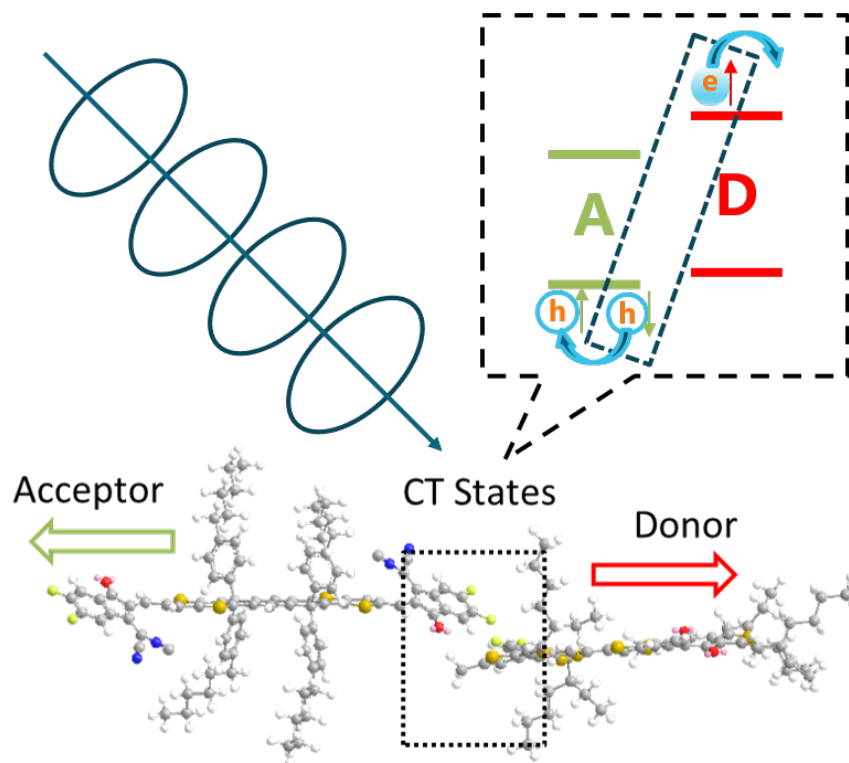
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Table of contents:

It is worth rethinking that the exciton separation and transport mechanism in the high-efficiency system differ from that of the fullerenes as the electron acceptor. The singlet excitons dominate the photocurrent contribution through the linearly and circularly polarized light and magnetic field effect test. This result is opposite to the case of the previous low-efficiency system.



Supporting Information

Dissociation of singlet excitons dominates photocurrent improvement in high-efficiency non-fullerene organic solar cells

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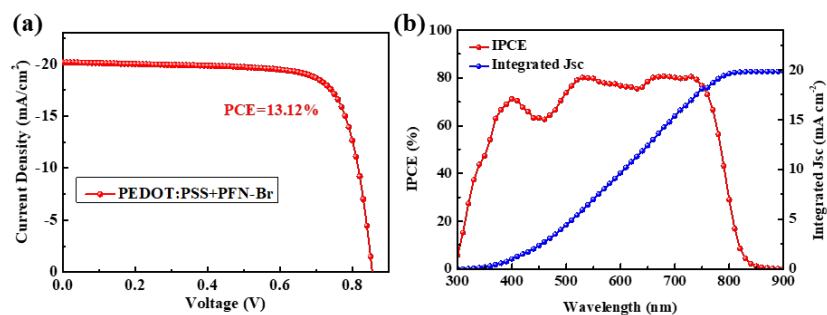


Figure S1(a) I-V curves of the device with different electron/hole transport layers. (b) the IPCE and the integral current curves of the device with PEDOT:PSS+PFN-Br.

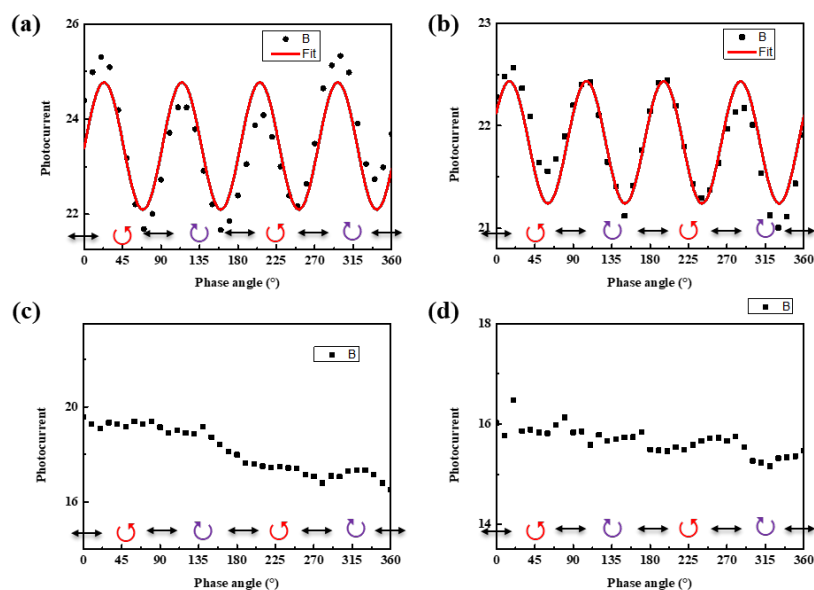


Figure S2 Photocurrent measured by switching phase angle under 1/2 wave plate (a) and 1/4 wave plate (b) of the PBDB-TF, Photocurrent measured by switching phase angle under 1/2 wave plate (c) and 1/4 wave plate (d) of the IT-4F.

Hosted file

image8.emf available at <https://authorea.com/users/580481/articles/621535-dissociation-of-singlet-excitons-dominates-photocurrent-improvement-in-high-efficiency-non-fullerene-organic-solar-cells>

Figure S3 the relationship of Raman intensity with different polarized angles.

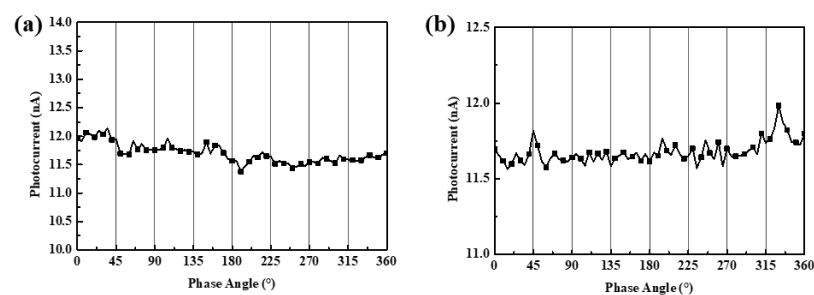


Figure S4 (a) Photocurrent measured by switching phase angle under 1/2 wave plate of the standard Si solar cell, (b) Photocurrent measured by switching phase angle under 1/4 wave plate of the standard Si solar cell.

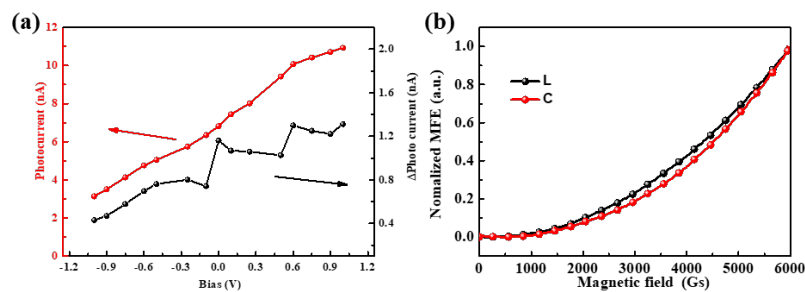


Figure S5 (a) The relationship of PC and [?]PC with different applied voltage. (b) Normalized linearly and circularly polarized photocurrents vary with the magnetic field.